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**Investigating the Microstructure of Poly(Cyclosilane) by 29Si Solid-State NMR Spectroscopy and DFT Calculations**

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Investigating the Microstructure of Poly(Cyclosilane) by 29Si Solid-State NMR Spectroscopy and DFT Calculations

Abstract
Using high-resolution magic-angle spinning (MAS) solid-state NMR spectroscopy and density-functional theory (DFT) calculations, we determine the microstructure of the silicon-based functional polymer poly(1,4Si6) arising from the dehydrocoupling polymerization of cyclosilane 1,4Si6. 1H-29Si refocused-INEPT experiments allow the unambiguous determination of the number of attached protons to a silicon atom for each 29Si signal in 1,4Si6 and poly(1,4Si6). One-dimensional 1H→29Si cross-polarization MAS (CPMAS) spectra of poly(1,4Si6) show the development of SiH resonances upon polymerization and peak integration indicates an average degree of polymerization of 20. The 1H→29Si CPMAS spectrum of poly(1,4Si6) also shows two sets of isotropic signals, suggesting the presence of at least two distinct species. Two-dimensional 29Si dipolar double-quantum-single-quantum and single-quantum-single-quantum homonuclear correlation spectra reveal similar connectivity in the two species, pointing to stereochemical and/or conformational heterogeneity. DFT calculations on trimer models predict that chair or twist-boat conformations and with cis or trans diastereomers are all energetic minima. 29Si chemical shift calculations of the lowest energy structures show that conformers and stereoisomers are expected to give rise to distinct 29Si NMR peaks and likely explain the appearance of multiple sets of 29Si NMR signals. The strategy outlined here is expected to be widely useful for the microstructural elucidation of silicon-based functional polymers.

Disciplines
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Investigating the Microstructure of Poly(Cyclosilane) by $^{29}\text{Si}$ Solid-State NMR Spectroscopy and DFT Calculations

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ABSTRACT:

Using high-resolution magic-angle spinning (MAS) solid-state NMR spectroscopy and density-functional theory (DFT) calculations, we determine the microstructure of the silicon-based functional polymer poly(1,4Si₆) arising from the dehydrocoupling polymerization of cyclosilane 1,4Si₆. ¹H-²⁹Si refocused-INEPT solid-state NMR experiments allow the unambiguous determination of the number of attached protons to a silicon atom for each ²⁹Si signal in 1,4Si₆ and poly(1,4Si₆). One-dimensional ¹H→²⁹Si cross-polarization MAS (CPMAS) NMR spectra of poly(1,4Si₆) show the development of SiH resonances upon polymerization and peak integration indicates an average degree of polymerization of 20. The ¹H→²⁹Si CPMAS spectrum of poly(1,4Si₆) also shows two sets of isotropic signals, suggesting the presence of at least two distinct species. Two-dimensional ²⁹Si dipolar double-quantum-single-quantum and single-quantum-single-quantum homonuclear correlation NMR spectra reveal similar connectivity in the two species, pointing to stereochemical and/or conformational heterogeneity. DFT calculations on trimer models predict that chair or twist-boat conformations and with cis or trans diastereomers are all energetic minima. ²⁹Si chemical shift calculations of the lowest energy structures show that conformers and stereoisomers are expected to give rise to distinct ²⁹Si NMR peaks and likely explain the appearance of multiple sets of ²⁹Si NMR signals. The strategy
outlined here is expected to be widely useful for the microstructural elucidation of silicon-based functional polymers.

**INTRODUCTION:**

The synthesis of silicon-based soft matter is a growing field, with representative achievements in colloidal nanocrystals\(^1\)\(^{-5}\), integrated nanocrystal-polymer hybrids,\(^5\)\(^{-7}\) donor-acceptor chromophores,\(^8\)\(^{-13}\) molecular electronics\(^{14}\)\(^{-19}\) and conjugated polymers,\(^20\)\(^{-26}\) with potential applications as photovoltaic and photonic devices.\(^5\)\(^{-6},\)\(^27\)\(^{-32}\) Recently, the dehydrocoupling polymerization of bifunctional cyclic precursors to provide polycyclosilanes has emerged as a route to functionalized polysilanes decorated with a periodic array of Si-Me and Si-H bonds (Scheme 1).\(^{24}\)\(^{-26},\)\(^{33}\) A comprehensive understanding of structure-function relationship facilitates development of next-generation materials. However, structural characterization of polysilanes can be challenging because poor solubility and a lack of long-range periodic order hinder solution NMR spectroscopy and X-ray diffraction studies, respectively. Additionally, characterization of molecular weight and molecular weight distribution is particularly challenging for inorganic polymers, given the differences in structure and hydrodynamic radius that complicate the use of size exclusion chromatography referenced to organic polystyrene standards.

High-resolution magic-angle spinning (MAS) solid-state NMR (SSNMR) spectroscopy is a powerful technique to probe microstructure and self-assembly in both organic and inorganic polymers.\(^{34}\)\(^{-40}\) Conventional one-dimensional (1D) \(^{13}\)C SSNMR spectroscopy provides information about the identity of the constitutional repeat units present in the polymer and can also be used to quantify and identify crystalline and amorphous domains.\(^{41}\)\(^{-46}\) NMR-active nuclei other than \(^{13}\)C may also be used to probe polymers by SSNMR spectroscopy. For example, \(^{11}\)B
SSNMR spectroscopy provided insight into the variable boron coordination environments in silicone boronate polymers.\textsuperscript{47} 1D $^{29}$Si SSNMR experiments have been previously used to characterize linear polysilanes, such as poly(dimethylsilylene),\textsuperscript{48-49} poly(di-$n$-hexylsilane)\textsuperscript{50} and poly(di-$n$-R$_x$silylene-co-di-$n$-R$_{x+1}$silylene) copolymers.\textsuperscript{51} More complex heteronuclear correlation (HETCOR), homonuclear correlation, spin diffusion and dipolar coupling measurement experiments are often required to fully understand the solid-state structure and dynamics of polymers.\textsuperscript{52-59}

Here, we present a strategy to determine key aspects of poly(cyclosilane) microstructure, including connectivity, tacticity and conformation. We contrast $^{29}$Si SSNMR spectra of cyclosilane 1,4Si$_6$ and the product of dehydrocoupling polymerization, poly(1,4Si$_6$) (Scheme 1). $^{29}$Si chemical shifts measured in 1D $^{29}$Si cross-polarization MAS (CPMAS) NMR spectra of 1,4Si$_6$ and poly(1,4Si$_6$) show the conversion of SiH$_2$ to SiH groups after polymerization, consistent with the proposed structure.\textsuperscript{24} Comparison of relative peak areas of the end groups and groups in the chain allow us to determine an average degree of polymerization of 20. Notably, we demonstrate $^1$H{$^{29}$Si} refocused INEPT experiments allow unambiguous determination of the number of attached proton atoms for each silicon NMR signal in both 1,4Si$_6$ and poly(1,4Si$_6$). Two-dimensional (2D) $^{29}$Si dipolar double-quantum-single-quantum (DQ-SQ) and SQ-SQ spin diffusion homonuclear correlation spectra illustrate the bonding and connectivity of the polymeric backbone. Finally, density-functional theory (DFT) calculations are used to construct simple trimer models of the polycyclosilanes and trends in calculated $^{29}$Si chemical shifts of the lowest energy structures are used to assign the observed sets of NMR signals to cis and trans stereoisomers with twist-boat and chair cyclohexasilane ring conformations.
Scheme 1. Dehydrocoupling polymerization of $1,4\text{Si}_6$. Inset shows single-crystal X-ray diffraction (SCXRD) structure of $1,4\text{Si}_6$.

**EXPERIMENTAL:**

*Synthesis.* $1,4\text{Si}_6$ and poly($1,4\text{Si}_6$) were synthesized as reported previously. GPC Analysis: $M_w = 5.74$ kDa, $M_n = 3.44$ kDa, $M_w/M_n = 1.67$. Gel permeation chromatography (GPC) was performed on a Tosoh Bioscience EcoSEC GPC workstation using butylatedhydroxytoluene stabilized tetrahydrofuran (THF) as the eluent (0.35 mL min$^{-1}$, 40 °C) through TSKgel SuperMultipore HZ-M guard column (4.6 mm ID x 2.0 cm, 4 μm, Tosoh Bioscience) and a TSKgel SuperMultipore HZ-M column (4.6 mm ID x 15 cm, 4μm, Tosoh Bioscience). Polystyrene standards (EasiVial PS-M, Agilent) were used to build a calibration curve. Processing was performed using EcoSEC Data Analysis software (Version 1.14, Tosoh Bioscience). Polymers were dissolved in THF (1 mg mL$^{-1}$), filtered (Millex-FGSyringeFilter Unit, 0.20 μm, PTFE, EMD Millipore), and injected using an auto-sampler (10 μL).

*Solid-State NMR Spectroscopy.* All SSNMR experiments were performed on a 9.4 T ($v_0(\text{H}) = 400$ MHz) Bruker wide-bore magnet spectrometer equipped with a Bruker Avance III HD console. SSNMR experiments were performed with either a Bruker 2.5 mm HXY MAS probe in triple resonance mode or a Bruker 4.0 mm HXY MAS probe configured in double resonance mode. All samples were packed into 2.5 mm and 4.0 mm zirconia rotors in a glove box under a nitrogen atmosphere and stored in the glovebox when not in use. Nitrogen gas was
used for all MAS experiments. Before each set of NMR experiments, the magic angle was precisely set by narrowing the second-order spinning sideband peak width of potassium bromide.\textsuperscript{60} 1H chemical shifts were referenced to neat tetramethylsilane using adamantane ($\delta_{\text{iso}}(\text{H}) = 1.82$ ppm) as a secondary chemical shift reference. \textsuperscript{29}Si chemical shifts were referenced indirectly using previously reported relative NMR frequencies.\textsuperscript{61} All NMR spectra were processed in Bruker Topspin 3.6.0.

1H longitudinal relaxation ($T_1$) measurements were performed on each sample using a saturation recovery experiment. All experiments were recorded with longitudinal relaxation delays of $1.3 \times T_1$ unless noted otherwise (Table S1). 1H radio frequency (RF) pulses were calibrated directly on each sample and \textsuperscript{29}Si RF pulses were calibrated with tetrakis(trimethylsilyl)-silane (TMSS). All 1H $\pi/2$ pulse widths were 2.5 $\mu$s (100 kHz RF field). 1H heteronuclear decoupling was performed during the indirect and direct acquisition of \textsuperscript{29}Si NMR signals with a ca. 100 kHz RF field and the SPINAL-64 decoupling sequence.\textsuperscript{62} Cross-polarization (CP) was directly optimized on each sample by monitoring the signal intensity of a $^{1}\text{H} \rightarrow ^{29}\text{Si}$ CPMAS spectrum for varying $^{1}\text{H}$ spin-lock RF fields while the $^{29}\text{Si}$ spin-lock RF field was held constant. X-detected (scalar, J-) refocused-INEPT,\textsuperscript{63-64} \textsuperscript{1}H-detected (scalar, J-) CP refocused-INEPT,\textsuperscript{63-65} CP-HETCOR,\textsuperscript{66} back-to-back (BABA) $^{1}\text{H}$ dipolar double-quantum-single-quantum (DQ-SQ) homonuclear correlation,\textsuperscript{67-69} single-quantum-single-quantum (SQ-SQ) $^{1}\text{H}$ spin diffusion homonuclear correlation with $^{1}\text{H}$ homonuclear decoupling applied during indirect dimension evolution,\textsuperscript{70-71} and DQ-SQ $^{29}\text{Si}$ homonuclear correlation with $R20_2^5$ homonuclear recoupling\textsuperscript{72} experiments were performed with the previously described pulse sequences.

eDUMBO\textsubscript{1-22} homonuclear dipolar decoupling\textsuperscript{73} was used in the CP-HETCOR, CP refocused-
INEPT and SQ-SQ homonuclear correlation experiments. Diagrams of all pulse sequences are shown in the Supporting Information (Figure S1).

1D CPMAS spectra were recorded on a Bruker 2.5 mm HXY probe with an MAS frequency of 25 kHz for $^{1,4}\text{Si}_6$ and a Bruker 4.0 mm HXY probe with an MAS frequency of 10 kHz for poly($^{1,4}\text{Si}_6$). CP for $^{1,4}\text{Si}_6$ was accomplished with a $^1\text{H}$ spin-lock RF field of ca. 63 kHz (85-100% amplitude ramp) and a $^{29}\text{Si}$ spin-lock RF field of ca. 40 kHz for a duration of 6 ms and for poly($^{1,4}\text{Si}_6$) with a $^1\text{H}$ spin-lock RF field of ca. 54 kHz (90-100% amplitude ramp) and a $^{29}\text{Si}$ RF field of ca. 42 kHz for a duration of 5.5 ms. The line-fitting module of NUTS NMR Processing Software (Acorn, Inc.) was used to fit the experimental CPMAS spin echo spectrum of poly($^{1,4}\text{Si}_6$). All 2D $^1\text{H}$-$^{29}\text{Si}$ HETCOR and refocused-INEPT experiments were acquired on a Bruker 2.5 mm HXY probe with an MAS frequency of ca. 22 kHz. eDUMBO $^{1-22}\text{homonuclear}$ $^1\text{H}$ dipolar decoupling$^{73}$ was implemented during the indirect acquisition of $^1\text{H}$ for the CP-HETCOR experiments to improve $^1\text{H}$ resolution and during the scalar ($J$-) coupling evolution times ($\tau$ and $\tau'$) in the CP refocused INEPT experiments to increase the $^1\text{H}$ coherence lifetime and slow $^1\text{H}$ spin diffusion. The initial phase and offset of eDUMBO$^{1-22}$ was optimized directly on each sample and used 32 $\mu$s pulse durations and 100 kHz RF fields. The eDUMBO$^{1-22}$ homonuclear dipolar decoupling scaling factor was determined to be 0.57 from a 2D $^1\text{H}$-$^1\text{H}$ SQ-SQ homonuclear correlation spectrum of poly($^{1,4}\text{Si}_6$) recorded with eDUMBO$^{1-22}$ applied during the $t_1$ evolution (Figure S2). The CP refocused-INEPT $\tau'$ curves were fit in MATLAB R2019a using the curve fitting application.

All 2D $^{29}\text{Si}$ homonuclear correlation experiments were performed on Bruker 4.0 mm HXY probe configured in double resonance mode at MAS frequencies of 6.25 kHz, 6.5 kHz, 6.75 kHz (SQ-SQ) and 6.25 kHz (DQ-SQ). The 2D $^{29}\text{Si}$ DQ-SQ homonuclear correlation
experiment used the \( R20^9 \) symmetry-based homonuclear dipolar recoupling sequence for DQ excitation and SQ reconversion.\(^{72}\) Composite 180° pulses consisting of a 90° and 270° pulse was implemented to enhance DQ efficiency and excitation bandwidth.\(^{72}\) \( ^{29}\)Si 90° and 270° pulse widths were 4.0 \( \mu \)s and 12.0 \( \mu \)s, respectively, corresponding to an RF field of 62.5 kHz. \( ^1\)H\(\rightarrow\)\( ^{29}\)Si CP was implemented at the start of the experiment to enhance sensitivity. CP was achieved with a \( ^1\)H spin-lock RF field of ca. 48 kHz (85-100\% amplitude ramp) and a \( ^{29}\)Si spin-lock RF field of ca. 42 kHz for a duration of 5.5 ms. The 2D \( ^{29}\)Si SQ-SQ homonuclear correlation experiments used rotational resonance recoupling to achieve \( ^{29}\)Si spin diffusion.\(^{74}\) 2D spectra were acquired with 1 second or 1 rotor period (1/MAS frequency) of \( ^{29}\)Si spin diffusion. \( ^1\)H\(\rightarrow\)\( ^{29}\)Si CP was implemented at the start of the experiment to enhance sensitivity. CP was achieved with a \( ^1\)H spin-lock RF field of ca. 57 kHz (6.25 kHz MAS), 53 kHz (6.5 kHz MAS) and 52 kHz (6.75 kHz MAS) and a corresponding \( ^{29}\)Si spin-lock RF field of ca. 43 kHz for all MAS frequencies, all for a duration of 7.1 ms and a 90-100\% \( ^1\)H RF field amplitude ramp.

*Density-Functional Theory Calculations.* All calculations were performed on the Gaussian09 package\(^{75}\) using density-functional theory with the B3LYP functional.\(^{76-79}\) The 6-31G** basis set was implemented for H,\(^{80-81}\) C\(^{81-82}\) and \( ^{29}\)Si\(^{83-84}\) atoms. All compounds were initially constructed using the open-source Avogadro molecular builder and visualization tool application.\(^{85}\) All structures were geometry optimized prior to NMR calculations. \( ^{29}\)Si chemical shielding values were calculated using the GIAO method and the same functional and basis set mentioned above. NMR calculations were performed on all trimer models with relative energies less than 5 kcal mol\(^{-1}\) and selected higher energy trimer models. \( ^{29}\)Si chemical shifts were calculated by converting calculated \( ^{29}\)Si chemical shielding values to \( ^{29}\)Si chemical shifts via a calibration plot (Figure S3). The \( ^{29}\)Si chemical shielding to chemical shift calibration plot was
obtained by calculating $^{29}\text{Si}$ chemical shielding values for compounds with previously reported $^{29}\text{Si}$ chemical shifts in solution (See Supporting Information). \cite{86,87}
RESULTS/DISCUSSION:

Figure 1. $^1$H→$^{29}$Si CPMAS spectra of (upper) 1,4Si$_6$ and (lower) poly(1,4Si$_6$) with the corresponding molecular structures. The methyl groups are omitted from the structure of poly(1,4Si$_6$) and only the chair conformer of the trans stereoisomer is shown for clarity. For poly(1,4Si$_6$), the $^{29}$Si spectrum was fit to six distinct isotropic peaks as summarized in Table 1.

1D $^{29}$Si CPMAS and 2D $^1$H-$^{29}$Si Solid-State NMR Spectra. The solid-state NMR spectra of 1,4Si$_6$ and poly(1,4Si$_6$) are discussed simultaneously. The previously published single-crystal X-ray diffraction (SCXRD) structure of 1,4Si$_6$ shows that the cyclosilane ring adopts a chair conformation (Scheme 1).$^{24}$ The $^1$H→$^{29}$Si CPMAS spectrum of 1,4Si$_6$ (Figure 1, upper) displays two sharp signals corresponding to the SiMe$_2$Si$_2$ (−39.5 ppm) and SiH$_2$Si$_2$ (−99.6 ppm) groups.
The sharp $^{29}$Si NMR signals reflect the highly-ordered, crystalline nature of the precursor. The $^{29}$Si NMR signals of 1,4Si$_6$ are observed at approximately the same chemical shift as they are in solution.$^{24-25}$ The assignment of these signals is confirmed by the relative peak intensities and also by $^1$H→$^{29}$Si CP-HETCOR and $^{29}$Si-$^1$H INEPT-HETCOR NMR experiments (Figure S4). eDUMBO$_{1,22}$ homonuclear dipolar decoupling$^{73}$ was used to enhance $^1$H resolution in the indirect dimension of the HETCOR NMR experiments and to extend the $^1$H coherence lifetime for $^1$H→$^{29}$Si INEPT coherence transfers. The 2D $^1$H→$^{29}$Si CP-HETCOR spectrum shows that both $^{29}$Si NMR signals correlate to $^1$H NMR signals at 0.4 and 3.0 ppm, attributed to SiCH$_3$ and SiH$_2$, respectively. Only the $^{29}$Si NMR signal at −99.6 ppm and the $^1$H NMR signal at 3.0 ppm are observed in the 2D $^{29}$Si-$^1$H INEPT-HETCOR spectrum, confirming the assignment of these signals to the SiH$_2$ residue.

We have previously demonstrated that the oscillation of $^1$H-$^{29}$Si refocused-INEPT NMR signals as a function of the time which $^{29}$Si transverse magnetization evolves under scalar ($J$-) coupling to $^1$H spins ($\tau'$) can be used to differentiate and quantify $^{29}$Si NMR signals from mono-, di- and tri-hydride groups that passivate the surface of silicon nano-crystals.$^{88}$ Here, the refocused-INEPT $\tau'$ curve conclusively shows that the SiH$_2$Si$_2$ signal of 1,4Si$_6$ arises from a silicon atom attached to two proton spins (Figure 2B, green curve). Excellent agreement is obtained when the $\tau'$ curve is fit solely to the function describing an SiH$_2$ spin system (Equation 1):

$$M_{SiH_2} = B \sin(4\pi J' \tau') e^{-\frac{2\tau'}{T_2'}}$$  \(1\)

where $B$ is a fitted constant to adjust the signal amplitude, $J'$ is the scaled Si-H $J$-coupling constant ($J' = 0.57 \times J$) and $T_2'$ is the $^{29}$Si refocused transverse relaxation time constant under
homonuclear decoupling. The fit of the $\tau'$ curve gives $T_{2}' = 17.0$ ms and $J' = 92$ Hz, which corresponds to $^{1}J_{\text{Si-H}} = 161$ Hz after accounting for the homonuclear decoupling scaling factor (Figure S2). The $^{1}J_{\text{Si-H}}$ of 161 Hz measured in the solid-state is in good agreement with that measured in solution ($^{1}J_{\text{Si-H}} = 170.1$ Hz).24

The $^{1}H\to^{29}Si$ CPMAS spin echo spectrum of poly(1,4Si$_6$) (Figure 1, lower) displays three broad signals and was fit to a total of six peaks. As discussed below, the splitting of each signal into two sets of peaks (denoted a and a’, b and b’, c and c’) is attributed to distinct microstructures present in the polymer chains. The broadening of the $^{29}Si$ NMR signals is reflective of structural disorder and lack of crystallinity typical of amorphous polymers. Each broad signal consists of two overlapped peaks, in roughly a 2:1 relative intensity based on the ratio of relative peak areas for both a:c and a’:c’ (Table 1). The signals in the region of –35 to –38 ppm (peaks a and a’) were assigned to SiMe$_2$Si$_2$ by analogy to 1,4Si$_6$. Signals between –100 to –102 ppm were assigned to SiH$_2$Si$_2$ (peaks b and b’) again by analogy to 1,4Si$_6$, however, in poly(1,4Si$_6$), the intensity of these signals is greatly reduced because SiH$_2$ groups are consumed upon polymerization. The $^{29}Si$ NMR signals with the most negative chemical shifts (~ –116 to –121 ppm) have no analog in 1,4Si$_6$ and were assigned to SiHSi$_3$ (mono-hydride, peaks c and c’) sites formed by linking two cyclosilane rings with the loss of hydrogen.

Further validation of the $^{29}Si$ chemical shift-based assignments came from 2D $^{1}H$-$^{29}Si$ HETCOR NMR spectra and a 2D $^{1}H$ DQ-SQ homonuclear correlation NMR spectrum (Figure S5). A 2D $^{1}H$-$^{29}Si$ HETCOR NMR spectrum of poly(1,4Si$_6$) was obtained with CP for the $^{1}H\to^{29}Si$ coherence transfer step (Figure 2A, blue). The $^{1}H$-$^{29}Si$ CP-HETCOR spectrum shows $^{29}Si$ NMR signals from both SiMe$_2$Si$_2$ and SiHSi$_3$ are correlated to $^{1}H$ NMR signals at ca. 0.5 ppm and 3 ppm, assigned to methyl groups and the mono-hydride, respectively. The CP-
HETCOR spectrum shows relayed correlations due to substantial $^1$H spin diffusion during the 5 ms contact time used for the $^1$H→$^{29}$Si CP transfer. A second HETCOR spectrum was also obtained with refocused-INEPT to perform a selective $^{29}$Si→$^1$H coherence transfer based upon $J$-couplings. The INEPT-HETCOR spectrum only shows the $^1$H and $^{29}$Si NMR signals associated with SiHSi$_3$ (Figure 2A, red). The $^1$H→$^{29}$Si refocused-INEPT $\tau'$ curve of poly(1,4Si$_6$) confirms the assignment of the $^1$H and $^{29}$Si NMR signals to the SiHSi$_3$ which features a single hydrogen attached to silicon (Figure 2B, red). The predicted curve was fit to Equation 2 which gives the oscillation of an SiH NMR signal:

$$M_{\text{SiH}} = A \sin(2\pi J' \tau') e^{-\frac{2\tau'}{T_2'}}$$  (2)

The fit of the $\tau'$ curve gives $T_2' = 7.0$ ms and $J' = 89$ Hz, which corresponds to $^1J_{\text{Si-H}} = 155$ Hz. The $^1J_{\text{Si-H}}$ of 155 Hz measured by SSNMR is in reasonable agreement with that measured in solution ($^1J_{\text{Si-H}} = 170.4$ Hz)$^{24}$ and is typical of $^1J_{\text{Si-H}}$ measured for silanes.$^{86}$
Figure 2. (A) (blue) 2D $^1$H→$^{29}$Si CP-HETCOR spectrum of poly($1,4$Si$_6$) overlaid on a (red) $^1$H-detected $^1$H{$^{29}$Si} INEPT-HETCOR spectrum of poly($1,4$Si$_6$). The CP-HETCOR spectrum was recorded with e-DUMBO$_{1-22}$ homonuclear dipolar decoupling during the $^1$H indirect dimension evolution period and a 5 ms contact time. The INEPT-HETCOR spectrum was recorded with e-DUMBO$_{1-22}$ homonuclear dipolar decoupling applied during the INEPT transfer and 1.6 ms and 2.24 ms $\tau$ and $\tau'$ mixing times, respectively (Figure S1A). (B) $^1$H{$^{29}$Si} refocused-INEPT $\tau'$ curves of (green) $1,4$Si$_6$ and (red) poly($1,4$Si$_6$). The black dots represent the experimental data points and the best fit curves are represented as solid lines. The dashed lines indicate zero amplitude for each curve. The curves were fit to the equations indicated in the main text. The equations vary depending on the number of hydrogens attached to the Si atom.
Peak Quantification and Chain Length Determination. The 1D $^{29}$Si CPMAS NMR spectra were recorded with relatively long CP contact times ($\tau_{CP} = 5.5$ and 6 ms for poly(1,4Si$_6$) and 1,4Si$_6$, respectively) to obtain quantitative $^{29}$Si NMR spectra. A long CP contact time promotes extensive $^1$H spin diffusion and maximizes magnetization transfer to both protonated and non-protonated $^{29}$Si sites. Indeed, integration of the two $^{29}$Si CPMAS NMR signals observed for 1,4Si$_6$ yields relative peak areas of 2.0:1.0 for the SiMe$_2$Si$_2$ to SiH$_2$Si$_2$, consistent with the molecular structure (Table 1). For poly(1,4Si$_6$), integration of the SiMe$_2$Si$_2$, SiH$_2$Si$_2$ and SiHSi$_3$ CPMAS NMR signals yield a relative integrated intensity ratio of 40:1:19 (Table 1). The approximate 2:1 integrated intensity ratio (40:19) for SiMe$_2$Si$_2$ and SiHSi$_3$ confirms that the $^{29}$Si CPMAS spectrum of poly(1,4Si$_6$) gives quantitative peak intensities. The 40:1:19 peak area ratio suggests a degree of polymerization of 20. Comparison of the fitted peak areas within the a:b:c and a’:b’:c’ sets both also yield an approximate average degree of polymerization of 20 (see discussion in Supporting Information).

NMR techniques complement size exclusion chromatography (SEC) for analysis of polymer molecular weight characterization. For many conjugated polymers, low solubility and a rigid backbone limit SEC’s effectiveness due to interactions between the polymer and column walls.\textsuperscript{89} SEC is also limited for polysilane characterization due to the difference in hydrodynamic radius between polysilanes and the polystyrene standard.\textsuperscript{90} In the present case, SEC predicts a $M_n$ of 3.44 kDa, or an average degree of polymerization of 12. The different results obtained from NMR integration and SEC highlights the value of complementary analytical techniques.
Table 1. $^{29}\text{Si}$ chemical shifts and relative peak areas for the $^{1}\text{H} \rightarrow ^{29}\text{Si}$ CPMAS spectra of $1,4\text{Si}_6$ and poly($1,4\text{Si}_6$).

<table>
<thead>
<tr>
<th>Group</th>
<th>Peak</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>Relative Peak Areas</th>
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<tr>
<td>$1,4\text{Si}_6$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiMe$_2$</td>
<td>a</td>
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<td>SiH$_2$</td>
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<td>1.0</td>
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<tr>
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<td></td>
<td></td>
<td></td>
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<td>SiMe$_2$</td>
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<td>c’</td>
<td>–120.7</td>
<td>11.7</td>
</tr>
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$^{29}\text{Si}$ Homonuclear Correlation Solid-State NMR Spectra. We sought to probe the origin of the multiple sets of overlapped signals (denoted a and a’, b and b’, c and c’) in the poly($1,4\text{Si}_6$) $^{29}\text{Si}$ SSNMR CPMAS spectrum. We hypothesize that the two overlapped signals most likely arise from distinct conformers or stereoisomers. Here, we performed $^{29}\text{Si}$ homonuclear correlation experiments to probe the possibility that conformational or stereochemical differences explain the observation of multiple groups of signals in the poly($1,4\text{Si}_6$) $^{29}\text{Si}$ SSNMR spectra. Homonuclear correlation SSNMR spectra are very powerful methods to probe structure within solids. $^{1}\text{H}$ homonuclear correlation spectra are commonly acquired for polymers to identify functional groups and to probe connectivity, ordering and phase segregation. However, natural abundance $^{13}\text{C}$ homonuclear experiments, such as refocused INADEQUATE, are often very challenging due to the low natural abundance of the $^{13}\text{C}$ nuclei. The natural abundance of $^{29}\text{Si}$ is ca. five times greater than $^{13}\text{C}$; consequently $^{29}\text{Si}$ homonuclear correlation experiments are up to ca. 25 times more sensitive than $^{13}\text{C}$ homonuclear correlation experiments. Previously, natural abundance $^{29}\text{Si}$ DQ-SQ homonuclear correlation spectra have been used to probe silicon spatial proximities in polyoligosiloxysilicones.
First, we utilized a $^{29}\text{Si}$ dipolar DQ-SQ experiment that used $R20^9$ symmetry-based homonuclear dipolar recoupling to generate and reconver $^{29}\text{Si}$ DQ coherence.\textsuperscript{72} The 2D $^{29}\text{Si}$ dipolar DQ-SQ spectrum shows correlations between spatially proximate (dipole-coupled) $^{29}\text{Si}$ spin pairs, with directly bonded pairs of silicon atoms giving rise to the most intense NMR signals. In a 2D DQ-SQ spectrum, peaks will appear in the indirect dimension at a frequency equal to the sum of chemical shifts of the correlated spins. The indirect dimension of poly(1,4Si\textsubscript{6}) shows two distinct sets of correlations, which are denoted by the red and blue lines in Figure 3A. The correlation patterned observed in the $^{29}\text{Si}$ dipolar DQ-SQ spectrum of poly(1,4Si\textsubscript{6}) is consistent with our hypothesis that the a-b-c and a’-b’-c’ signals correspond to structurally similar species with unique microstructures. The 2D $^{29}\text{Si}$ dipolar DQ-SQ spectrum shows that both SiMe\textsubscript{2}Si\textsubscript{2} peaks have SiMe\textsubscript{2}Si-SiMe\textsubscript{2}Si autocorrelations (i.e., a-a and a’-a’ only). The SiMe\textsubscript{2}Si\textsubscript{2} peaks are also correlated to only the SiHSi\textsubscript{3} peaks within a set (i.e., a-c and a’-c’ correlations). However, correlations illustrating the Si\textsubscript{3}HSi-SiHSi\textsubscript{3} linkages could not be clearly observed in the DQ-SQ spectrum due to the low sensitivity of the experiment and unfavorable relaxation of the SiHSi\textsubscript{3} signal under $^{29}\text{Si}$ homonuclear recoupling. While a weak Si\textsubscript{3}HSi-SiHSi\textsubscript{3} c-c autocorrelation is present for the most intense hydride signal, because of the low signal-to-noise ratio we cannot rule out the possibility of c-c’ or c’-c’ correlations.
Figure 3. (A) 2D $^{29}$Si dipolar double-quantum-single-quantum (DQ-SQ) spectrum of poly(1,4Si$_6$). The blue and the red lines show the Si-Si bonding of two distinct microstructures. (B) 2D $^{29}$Si rotational resonance recoupled spin diffusion SQ-SQ spectra of poly(1,4Si$_6$) acquired with (red) 1 rotor period ($\nu_{\text{rot}} = 6.5$ kHz) of spin diffusion or (black) 1 second of spin diffusion. (C) Extracted rows from the 1 second spin diffusion 2D spectrum. The color of the extracted spectrum corresponds to the initial magnetization starting at the same colored peak in the CPMAS spectrum from Figure 1.
To probe the linkage between cyclosilanes and resolve the issue of low sensitivity in the DQ-SQ experiment, we used rotational resonance recoupling to enable $^{29}$Si homonuclear spin diffusion and record a 2D $^{29}$Si SQ-SQ homonuclear correlation spectrum. Although both DQ-SQ and SQ-SQ experiments will probe and identify proximate $^{29}$Si spin pairs, the $^{29}$Si spin diffusion SQ-SQ experiment provides much better sensitivity because relaxation during the recoupling time is governed by the $^{29}$Si longitudinal relaxation time ($T_1$), while for DQ-SQ experiments the much shorter $^{29}$Si homogenous effective transverse relaxation ($T_2'$) controls relaxation during recoupling. Rotational resonance was achieved by setting the MAS frequency to 6.5 kHz to match the frequency difference between the middle of the SiMe$_2$Si$_2$ $^{29}$Si NMR signal and the middle of the SiHSi$_3$ $^{29}$Si NMR signal. Additionally, broadening of the $^{29}$Si NMR signals by $^1$H heteronuclear couplings (dipolar and scalar) should also help accelerate $^{29}$Si spin diffusion by proton-driven spin diffusion. 2D $^{29}$Si SQ-SQ correlation spectra of poly(1,4Si$_6$) were recorded with spin diffusion time periods of 154 $\mu$s (one rotor period) or 1 second (Figure 3B). Analysis of the reference 2D spectrum (1 rotor period of $^{29}$Si spin diffusion) clearly shows all signals lie on the diagonal (indicated by the dashed line). When the $^{29}$Si spin diffusion time is increased to 1 second, off-diagonal correlations resulting from homonuclear $^{29}$Si spin diffusion are also visible. Rows were extracted from the indirect dimension at the isotropic $^{29}$Si chemical shifts for the a, a’, c’ and c signals (Figure 3C). Analysis of the rows suggest that $^{29}$Si spin diffusion more likely occurs within a set of peaks, i.e. a↔c and a’↔c’ spin diffusion is more likely than a↔c’ or a’↔c. This observation is in agreement with the DQ-SQ spectrum which suggested that the two sets of signals arise from structurally similar species with unique microstructures. We note that after 1 second of $^{29}$Si spin diffusion there is no indirect dimension broadening of the $^{29}$Si NMR
signals lying on the diagonal, suggesting that $a\leftrightarrow a'$ and $c\leftrightarrow c'$ $^{29}\text{Si}$ spin diffusion has not occurred, which is also consistent with spatial segregation of the two sets of macromolecules.

We performed two additional 2D $^{29}\text{Si}$ SQ-SQ rotational resonance recoupled spin diffusion experiments with MAS frequencies of 6.25 kHz and 6.75 kHz to match the frequency differences between the $a'$-c' and a-c peaks, respectively (Figure S6-S7). These extra experiments confirm that $^{29}\text{Si}$ spin diffusion more likely occurs within a set of peaks (i.e. $a\leftrightarrow c$ and $a'\leftrightarrow c'$) and was not biased by the chosen MAS frequency of 6.5 kHz, corroborating our observations above and suggesting the presence of at least two distinct polymer microstructures.

**DFT Predicted Microstructures and $^{29}\text{Si}$ Chemical Shifts.** Both stereochemical and conformational heterogeneity are plausible explanations for the appearance of multiple isotropic signals in the $^{29}\text{Si}$ CPMAS NMR spectrum of poly($1,4\text{Si}_6$). While poly($1,4\text{Si}_6$) is a highly symmetric, achiral structure, the $\text{SiHSi}_3$ sites linking internal cyclosilane rings are pseudoasymmetric centers. A simplified trimer model showing the cis/trans isomerism at the central ring, as well as the Cahn–Ingold–Prelog (CIP) stereodescriptors for pseudoasymmetric centers, is shown in Figure 4 and Figure S8, respectively.
Figure 4. Illustration of cis/trans isomerism in 1,4Si₆ trimers and a corresponding conformer for each diastereomer resulting from an internal ring inversion. The red and blue H atoms denote cis and trans isomerism, respectively. Equatorial (Eq, green) and axial (Ax, orange) cyclosilane linkages are labeled. Methyl groups omitted for clarity.

Furthermore, a number of conformers exist for each stereoisomer. Each cyclosilane ring within a trimer may adopt a chair or twist-boat (twist) conformation and ring inversion inverts axial and equatorial substituents (Figure 4). Prior work has identified significant populations of twist conformers in cyclosilanes at room temperature in addition to the most favorable chair conformer,⁹⁸–⁹⁹ an observation unique to Si₆R₁₂ species, as cyclohexane populates nearly exclusively the chair conformation at room temperature. The free energy profile of cyclohexane ring inversion is well known: chair and twist conformers are energetic minima that differ in energy by 5–6 kcal mol⁻¹ and the boat conformation is a transition state between “chair flips”.

The profile of cyclohexasilane ring inversion is much flatter. Smaller energy differences between
chair and twist conformers and smaller barriers to ring inversion have been calculated. For example, solid-state Raman spectra of dodecamethylcyclohexasilane (Si$_6$Me$_{12}$) detected contributions from twist conformations at room temperature, while non-chair conformers of cyclohexane are typically only observed above 800 °C. Indeed, DFT calculations of chair and twist monomer structures predict that the twist conformer is only 1.97 kcal mol$^{-1}$ higher in energy (Figure 5A and 5B).

While conformational effects and tacticity are not mutually exclusive, the observation of multiple $^{29}$Si peaks in both solution and solid-state NMR spectra of poly(1,4Si$_6$) points to stereoisomerism as a significant contributor. Conformational exchange is often rapid in solution, therefore, if conformational change alone was contributing, significant differences between solution and solid-state NMR spectra would be expected. Tacticity in polyhydrosilanes has been investigated previously and the Cp$_2$ZrCl$_2$/n-BuLi catalyst system used herein yields atactic polyphenylsilanes, further supporting the probability of stereoisomerism.

DFT calculations were performed on trimer models to elucidate the three dimensional structure of the poly(1,4Si$_6$) chain and explain the appearance of multiple sets of $^{29}$Si NMR signals. We calculated trimers with two isomeric configurations (trans or cis arrangement of hydrides on the central ring) and conformers focusing on chair/twist ring conformations and equatorial-equatorial, equatorial-axial or axial-axial linkages. Boat conformations were not considered because during geometry optimization they convert to twist conformations. $^{29}$Si chemical shifts were then calculated for the lowest energy structures (less than 5 kcal mol$^{-1}$ relative energy, Table S2-S3 and Figure S9).

The most stable structure was the trans-diastereomer in which all rings were in chair conformations and in the equatorial position (Eq-Eq), as well as in a staggered arrangement.
= 0.0 kcal mol\(^{-1}\), Figure 5D). The second lowest energy structure was the cis-diastereomer with cyclosilane rings in chair-twist-chair (CTC) conformations. All cyclosilanes were in equatorial or psueodequatorial positions (Eq-Eq) (\(E_{\text{rel}} = +1.9\) kcal mol\(^{-1}\), Figure 5E). Numerous other energetically stable structures (10 total) were predicted (\(E_{\text{rel}} < +5.0\) kcal mol\(^{-1}\)), with most featuring Eq-Eq linkages and either all rings in the chair conformation or a single twisted ring (Table S2 and Figure S9).
Figure 5. DFT geometry optimized monomers possessing (A) chair and (B) twist cyclosilane ring conformations and trimer models with all Eq-Eq linkages and the cyclosilane rings in the (D) all chair (trans) and (E) chair-twist-chair (CTC, cis) conformations. (C, F) DFT calculated $^{29}\text{Si}$ chemical shifts of the (C) monomer and (F) trimer models overlaid on the experimental CPMAS spectra from Figure 1 of 1,4Si$_6$ and poly(1,4Si$_6$), respectively. The colors of the silicon atoms in the structural models correspond to the color of the calculated $^{29}\text{Si}$ peak positions. DFT calculated $^{29}\text{Si}$ peaks were broadened and their amplitudes were scaled to match that of the experimental spectrum for illustration purposes.

$^{29}\text{Si}$ chemical shifts were calculated for the cyclosilane monomers and the 10 lowest energy trimer structures with relative energies within $+5.0$ kcal mol$^{-1}$ and additional select higher energy trimers (Table S3 and S4). Both ring conformation and cis/trans isomerism influence $^{29}\text{Si}$
chemical shifts (Figure 5 and Figure S9). There is poor agreement between the predicted and observed \(^{29}\text{Si}\) isotropic chemical shifts for all structures, despite the fact that the shielding to chemical shift calibration curve obtained for model compounds predicts that the calculated \(^{29}\text{Si}\) isotropic chemical shifts should be within ca. 5.4 ppm of the experimental shifts (Table S5). The differences between the observed and predicted chemical shifts likely arise because the simplified trimer models neglect intramolecular packing interactions.

While the absolute agreement between experimental and predicted \(^{29}\text{Si}\) chemical shifts are poor, there is reasonable agreement between the relative experimental and predicted \(^{29}\text{Si}\) chemical shifts for the two lowest energy trimer structures (Figure 5F and Table S3). The \(^{29}\text{Si}\) chemical shifts for the lowest energy \textit{trans}-diastereomer (all Eq-Eq linkages, all chair rings) are predicted to occur at –113.1 ppm for the mono-hydride group and –10.7 ppm for the SiMe\(_2\)Si\(_2\) group. The \(^{29}\text{Si}\) chemical shift for the higher energy \textit{cis}-diastereomer (all Eq-Eq linkages, CTC ring conformations) are predicted to occur at –109.4 ppm for the mono-hydride group and –17.3 ppm for the SiMe\(_2\)Si\(_2\) group. Importantly, the pattern in the predicted \(^{29}\text{Si}\) chemical shifts is consistent with the experimentally observed peak intensities and connections observed in the 2D \(^{29}\text{Si}\) homonuclear correlation NMR spectra which suggested the higher frequency SiMe\(_2\)Si\(_2\) signal and lower frequency mono-hydride signal are correlated and vice-versa (a-c and a’-c’ groups). In addition, the lowest energy trimer (all Eq-Eq chair, \textit{trans} isomer) was predicted to have the higher SiMe\(_2\)Si\(_2\) and lower mono-hydride \(^{29}\text{Si}\) chemical shifts (signals a and c). The correlation between the predicted energy of the structure, peak intensities and predicted shifts lends credence to the structural models, suggesting that the two sets of signals most likely arise from stereoisomers. Multiple \(^{29}\text{Si}\) NMR signals were also observed in solution NMR spectra of poly(1,4Si\(_6\)), despite the fact that conformational dynamics are expected to be much more rapid.
in solution. Therefore, based upon the observation of distinct sets of $^{29}$Si NMR signals in solution and solid-state NMR spectra and DFT modeling, we hypothesize that the two sets of $^{29}$Si signals arises from trans and cis diastereomers with chair and twist cyclosilane ring conformations that are likely randomly distributed within the polymer chains.

CONCLUSION:

$^1$H and $^{29}$Si MAS SSNMR spectroscopy is an ideal technique to probe the microstructure of silicon-based polymers. $^1$H→$^{29}$Si CPMAS SSNMR experiments show the transformation of the SiH$_2$Si$_2$ groups on 1,4Si$_6$ to SiHSi$_3$ groups on poly(1,4Si$_6$). Integration of the SiMe$_2$Si$_2$, SiH$_2$Si$_2$ and SiHSi$_3$ signals in the CPMAS spin echo spectrum of poly(1,4Si$_6$) revealed an average degree of polymerization of 20. $^1$H→$^{29}$Si refocused-INEPT signal oscillations unambiguously confirm that 1,4Si$_6$ consist of di-hydride species and poly(1,4Si$_6$) consist predominantly of mono-hydride species. 2D $^1$H-$^{29}$Si HETCOR experiments with CP and INEPT for the $^1$H→$^{29}$Si coherence transfer and natural isotopic abundance $^{29}$Si DQ-SQ and SQ-SQ homonuclear correlation experiments confirm the $^{29}$Si chemical shift assignments of the SiMe$_2$Si$_2$, SiH$_2$Si$_2$ and SiHSi$_3$ groups and the bonding of the different fragments, allowing for determination of the molecular structure. The connectivity patterns observed in the 2D $^{29}$Si homonuclear correlation spectra suggest that there are two distinct microstructures present in poly(1,4Si$_6$). Lastly, DFT calculations of simplified trimer models were used to determine energies of possible conformations/stereoisomers and predict the $^{29}$Si chemical shifts for the low energy structures. The DFT calculations predict that the two most stable trimers correspond to the trans ($E_{\text{rel}} = 0.0$ kcal mol$^{-1}$) and cis ($E_{\text{rel}} = +1.9$ kcal mol$^{-1}$) diastereomers. While the predicted $^{29}$Si chemical shifts showed relatively poor agreement with the experimental data, the predicted
energies and relative $^{29}$Si chemical shift differences allow us to speculate that the splitting of the $^{29}$Si NMR signals for poly(1,4Si$_6$) occurs due to trans and cis diastereomers, where the trans-diastereomers would likely adopt the all Eq-Eq chair conformation and the cis-diastereomers would likely adopt the all Eq-Eq CTC conformation.

This study supports the future optimization of structure-property relationships by revealing key details of polycyclosilane microstructure. Future work will target the preparation of stereoregular poly(cyclosilane) via catalyst control.\textsuperscript{103-106} The relationship between synthesis conditions and polymer molecular weight will also be investigated, although, dehydrogenative silane polymerization is an example of a step-growth condensation polymerization and inefficient removal of hydrogen is typically thought to limit conversion to high molecular weight polymers.\textsuperscript{33, 107} Finally, the approaches outlined here should be useful to determine the molecular structure, conformation and connectivity of other silicon-based polymers.

**Supporting Information:**

The Supporting Information is available free of charge on the ACS Publications website.

- Additional solid-state NMR spectra, solid-state NMR experimental parameters, DFT calculated energies, DFT calculated $^{29}$Si chemical shifts of low energy structures and DFT calculated atomic coordinates of all cyclosilane models.

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